Attorney Docket No. 05725.1243
Customer No. 22,852

UNITED STATES PATENT APPLICATION

FOR

NAIL VARNISH COMPOSITION COMPRISING A BLOCK POLYMER

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[001] This application claims priority under 35 U.S.C. §119 of Application No. 0211949, filed September 26, 2002, Application No. 0216437, filed December 20, 2002, and Application No. 0306121, filed May 21, 2003, in France, all of which are incorporated herein by reference.

[002] The present invention relates to a nail varnish composition comprising at least one block polymer. The invention also relates to a makeup or care process for the nails.

[003] Compositions to be applied, for example to the nails, such as solvent-based nail varnishes or nailcare bases, usually comprising at least one film-forming polymer, optionally at least one plasticizer, pigments, rheological agents and solvents, are known.

[004] At the present time, nitrocellulose is the film-forming agent most widely used in solvent-based nail varnishes in formulations with optimized gloss and staying power.

[005] Formulations comprising nitrocelluloses may make it possible to obtain films with a satisfactory level of hardness and gloss, but the formulations may lack adhesion to the nail. This drawback may be overcome by adding plasticizers, but the addition of plasticizers or co-resins to such formulations generally requires that they be added in very large amounts, on the order of those of the nitrocellulose.

[006] Furthermore, the presence of plasticizers in these formulations may be reflected, after formation of the film and drying, by a change in the properties of the film over time. This may be due both to a slow evaporation of the residual solvents contained in the film after drying and to a potential loss of some of the plasticizers, for

example by evaporation, leading to hardening of the film over time and poor chip resistance of the film.

[007] The research efforts made towards replacing nitrocellulose with other film-forming agents, such as polyacrylics and polyurethanes, in nail varnishes - for instance the aqueous polyurethane dispersions described in document EP 0 648 485 - have not given completely satisfactory results, for example, in terms of staying power and resistance to external factors, such as water or detergents.

[008] The present inventors have discovered, surprisingly, that a nail varnish composition with a tangent delta (tgδ) dampening power of greater than or equal to 0.4 makes it possible to obtain at least one of the following properties, while at the same time producing a film of glossy composition:

[009] - plasticization of the resulting film without needing to add large amounts of external plasticizers, while at the same time maintaining a good level of hardness of the film, and

[010] - good impact strength and/or chip strength of the nail varnish composition and therefore an improvement in the staying power of the varnishes on the nail over time and/or in their wear resistance.

[011] Disclosed herein is a nail varnish composition comprising, in a cosmetically acceptable medium comprising at least one organic solvent, at least one block polymer, the composition being capable of forming a film with a tangent delta (tgδ) dampening power of greater than or equal to 0.4 at a temperature of 30°C and a frequency of 20 Hz.

[012] As defined herein, the expression "cosmetically acceptable medium" means a non-toxic medium that may be applied to at least one of human skin, integuments, and the lips of the face.

[013] Also disclosed herein is a cosmetic non-therapeutic makeup or care process for the nails, comprising applying to the nails one coat of the nail varnish composition as defined above.

[014] Further disclosed herein is a method for producing a glossy film comprising applying to nails a nail varnish composition comprising at least one block polymer, the composition being capable of forming a film with a tangent delta (tgδ) dampening power of greater than or equal to 0.4 at a temperature of 30°C and a frequency of 20 Hz, wherein a glossy film is produced with at least one of good staying power and good wear resistance.

[015] The at least one block polymer disclosed herein may be formulated as a sole film-forming polymer or may be combined with at least one standard film-forming polymer, for example nitrocellulose or a cellulose derivative, without having the drawback, in the case of a cellulose derivative, of adding large amounts of plasticizers.

[016] The composition disclosed herein may be capable of forming a film having viscoelastic behavior.

[017] In general, a material may be viscoelastic when, due to the effect of shear, it has both the characteristics of a purely elastic material, i.e., it is capable of storing energy, and the characteristics of a purely viscous material, i.e., it is capable of dissipating energy, and for which the response to stresses is a function of time (non-instantaneous response).

[018] The film of the composition disclosed herein may be characterized by its dampening power tgδ, which is defined as the ratio between the dissipated energy and the transmitted energy in the material.

[019] The composition disclosed herein may be capable of forming a film with a dampening power tgδ of greater than or equal to 0.4, for example ranging from 0.4 to 1.5, in an embodiment greater than or equal to 0.5, for example ranging from 0.5 to 1.5, and in another embodiment greater than or equal to 0.6, for example ranging from 0.6 to 1, at a temperature of 30°C and a frequency of 20 Hz. Moreover, the composition disclosed herein may be capable of forming a film with a storage modulus E' of greater than or equal to 1 MPa, for example ranging from 1 MPa to 5000 MPa, in one embodiment greater than or equal to 5 MPa, for example ranging from 5 to 1000 MPa, and in another embodiment greater than or equal to 10 MPa, for example ranging from 10 to 500 MPa, at a temperature of 30°C and a frequency of 0.1 Hz.

Methods for measuring the characteristics of the film obtained with the inventive composition

[020] The dampening power tgδ is measured by DMTA (Dynamic and Mechanical Temperature Analysis).

[021] To measure the dampening power tgδ of the film of the composition, viscoelasticimetry tests are performed using a DMTA machine from Polymer TA Instruments (model DMA2980) on a sample of film of the composition. The sample is prepared by pouring the composition into a Teflon-coated mold, followed by drying on a plate thermostatically maintained at 30°C for 24 hours, under ambient humidity conditions (such as 50% ± 15% RH). Specimens are then cut from the film thus obtained (for example using a sample punch). These specimens may be about 200 μm

thick, about 5 to 10 mm wide and have a working length of about 10 to 15 mm, after drying for 24 hours.

[022] The measurements are performed at a constant temperature of 30°C.

[023] The sample is subjected to a tensile stress and small strains (for example, a sinusoidal displacement of ± 8 μm is applied thereto) during frequency scanning, the frequency ranging from 0.1 to 20 Hz. The process is thus performed in the linear domain, with small levels of strain.

[024] From these measurements, the complex modulus $E^* = E' + iE''$ of the film of the test composition may be determined, wherein E' is the storage modulus and E'' is the loss modulus. From these measurements, the dampening power: $tg\delta = E''/E'$, is also deduced.

[025] The composition disclosed herein may be, for example, capable of forming a film having a breaking strain of greater than or equal to 5%, for example ranging from 5% to 500%, and in an embodiment greater than or equal to 15%, for example ranging from 15% to 400%, and/or a breaking energy per unit volume Wr of greater than or equal to 0.2 J/cm^3, for example ranging from 0.2 to 100 J/cm^3, and in an embodiment greater than 1 J/cm^3, for example ranging from 1 to 50 J/cm^3.

[026] The breaking strain and the breaking energy per unit volume are determined by tensile tests performed on a film of the composition about 200 μm thick. The film is obtained by pouring the composition onto a Teflon-coated mold, followed by drying on a plate thermostatically maintained at 30°C for 7 days, under ambient humidity conditions (such as 50% ± 15% RH). To perform these tests, the film is cut into, for example, dumbbell-shaped specimens with a working length of 33 ± 1 mm and

a working width of 6 mm. The cross section (S) of the specimen is then defined as: S = width x thickness (cm^2); this cross section will be used to calculate the stress.

[027] The tests are performed, for example, on a tensile testing machine sold under the name LLOYD® LR5K. The measurements are performed at 20°C.

[028] The specimens are pulled at a travelling speed of 33 mm/minute, corresponding to a rate of 100% elongation per minute.

[029] A travelling speed is thus applied and the elongation ΔL of the specimen and the force F required to apply this elongation are simultaneously measured. From these data ΔL and F, the stress σ and strain ε parameters are determined.

[030] A curve of stress $\sigma = (F/S)$ as a function of the strain $\varepsilon = (\Delta L/Lo) \times 100$ is thus obtained. The test is conducted until the specimen breaks, wherein Lo is the initial length of the specimen.

[031] The breaking strain is the maximum strain of the sample before the breaking point (in %).

[032] The breaking energy per unit volume (Wr) in J/cm^3 is defined as the area under this stress/strain curve such that:

$$W_r = \int_0^{??} \sigma.\varepsilon.d\varepsilon$$

[033] 1) Block Polymer

[034] The at least one block polymer of the composition disclosed herein may be, for example, a film-forming linear block ethylene polymer.

[035] For purposes of the invention, the term “ethylene polymer” is understood to mean a polymer obtained by the polymerization of monomers containing an ethylenically unsaturated group.

[036] The term “block polymer” is understood to mean a polymer containing at least two separate blocks, for example at least three separate blocks.

[037] The block polymer may be a polymer with, for example, a linear structure. In contrast, a polymer having a non-linear structure may be, for example, a polymer with a branched, star, grafted or other structure.

[038] The term “film-forming polymer” is understood to mean a polymer capable of forming, by itself or in the presence of at least one auxiliary film-forming agent, a continuous film that adheres to a support, for example, to keratinous materials.

[039] The at least one block polymer of the composition according to the present invention comprises at least one first block and at least one second block that have different glass transition temperatures (Tg). The at least one first and second blocks may be linked together via at least one intermediate segment comprising at least one constituent monomer of the at least one first block and at least one constituent monomer of the at least one second block. In one embodiment, the at least one first block and the at least one second block are incompatible with each other.

[040] The expression blocks "that are incompatible with each other" means that the mixture of the polymer formed by the at least one first block and the polymer formed by the at least one second block (hereinafter referred to as “the polymer mixture”) is immiscible in the main polymerization organic solvent of the block copolymer at room temperature (25°C) and atmospheric pressure (10^5 Pa), at a content of the polymer

mixture greater or equal to 5% by weight of the total weight of polymers and solvent, and wherein

[041] (i) the polymer formed by the at least one first block and the polymer formed by the at least one second block are present in the polymer mixture in a ratio ranging from 10/90 to 90/10 by weight, and

[042] (ii) each of the polymer formed by the at least one first block and the polymer formed by the at least one second block has an average molar mass (weight-average or number-average molar mass) equal to the average mass of the block polymer +/- 15%.

[043] The expression "main polymerization organic solvent" means, in the case where there is a mixture of polymerization solvents, the polymerization solvent which has the highest content by weight relative to the total weight of the organic polymerization solvents. In the case where there is a mixture of polymerization solvents and two or more of the solvents are present in identical weight ratios, the polymer mixture is immiscible in at least one of the solvents. In the case where the polymerization is made in a single solvent, the single solvent is the main solvent.

[044] The at least one intermediate segment may be a block comprising at least one constituent monomer of the at least one first block and at least one constituent monomer of the at least one second block of the polymer and allows these blocks to be "compatibilized."

[045] In one embodiment, the at least one block polymer does not comprise any silicon atoms in its skeleton. The term "skeleton" means the main chain of the polymer, as opposed to the pendent side chains.

[046] In one embodiment, the polymer disclosed herein is not water-soluble, that is to say the polymer is not soluble in water or in a mixture of water and linear or branched lower monoalcohols having from 2 to 5 carbon atoms, such as ethanol, isopropanol, or n-propanol, without pH modification, with an active material content of less than 1% by weight, at room temperature (25°C).

[047] In one embodiment, the at least one block polymer is not an elastomer.

[048] The expression "non-elastomeric polymer" means a polymer which, when submitted to a stretching stress (for example when stretched by 30% of the original length) does not return to approximately its original length when released. Specifically, "non-elastomeric polymer" means a polymer with an instantaneous recovery $R_i < 50\%$ and a delayed recovery $R_{2h} < 70\%$ after having undergone a 30% elongation. In one embodiment, R_i is < 30% and R_{2h} is < 50%.

[049] More specifically, the elastomeric nature of the polymer may be determined according to the following protocol:

[050] A polymer film is prepared by pouring a solution of the polymer into a Teflon-coated mold followed by drying for 7 days under ambient conditions regulated to 23 ± 5°C and 50 ± 10% relative humidity. A film about 100 μm thick is thus obtained, from which are cut for example rectangular specimens (for example using a punch) 15 mm wide and 80 mm long. This sample is subjected to a tensile stress using a machine sold under the reference Zwick, under the same temperature and humidity conditions as for the drying operation. The specimens are drawn at a speed of 50 mm/minute and the distance between the jaws of the machine is 50 mm, which corresponds to the initial length (Lo) of the specimen.

[051] The instantaneous recovery R_i is determined in the following manner:

[052] The specimen is stretched by 30% (ε_{max}), i.e., about 0.3 times its initial length (Lo). The stress is released by applying a return speed equal to the tensile speed, i.e., 50 mm/minute, and the residual elongation percentage of the specimen, after returning to zero stress (ε_i), is measured.

[053] The percentage instantaneous recovery (R_i) is given by the formula below:

$$R_i = ((\varepsilon_{max} - \varepsilon_i)/ \varepsilon_{max}) \times 100$$

[054] To determine the delayed recovery, the residual percentage degree of elongation (ε_{2h}) of the specimen is measured 2 hours after returning to zero stress.

[055] The delayed percentage recovery in % after 2 hours (R_{2h}) is given by the formula below:

[056] $R_{2h} = ((\varepsilon_{max} - \varepsilon_{2h})/ \varepsilon_{max}) \times 100$

[057] For example, in one embodiment, the at least one block polymer of the composition disclosed herein has an instantaneous recovery R_i of 10% and a delayed recovery R_{2h} of 30%.

[058] The at least one block polymer disclosed herein comprises at least one first block and at least one second block that have different glass transition temperatures (Tg); the at least one first and second blocks being linked together via at least one intermediate segment comprising at least one constituent monomer of the at least one first block and at least one constituent monomer of the at least one second block.

[059] It is pointed out that, in the text hereinabove and hereinbelow, the terms "first" and "second" blocks do not in any way condition the order of the blocks in the structure of the polymer.

[060] The polydispersity index of the polymer disclosed herein may be greater than 2, for example ranging from 2 to 9, in one embodiment greater than or equal to 2.5, for example ranging from 2.5 to 8, and in another embodiment greater than or equal to 2.8, and for example ranging from 2.8 to 6.

[061] The polydispersity index I of the polymer may be equal to the ratio of the weight-average mass Mw to the number-average mass Mn.

[062] The weight-average (Mw) and number-average (Mn) molar masses are determined by gel permeation liquid chromatography (THF solvent, calibration curve established with linear polystyrene standards, refractometric detector).

[063] The weight-average mass (Mw) of the polymer disclosed herein may be, for example, less than or equal to 300,000, for example ranging from 35,000 to 200,000, and as a further example, ranging from 45,000 to 150,000.

[064] The number-average mass (Mn) of the polymer disclosed herein may be less than or equal to 70,000, for example ranging from 10,000 to 60,000, and as a further example, ranging from 12,000 to 50,000.

[065] Each block of the at least one block polymer of the composition disclosed herein may be derived from one type of monomer or from several different types of monomers.

[066] This means that each block may comprise a homopolymer or a copolymer. This copolymer constituting the block may in turn be random or alternating.

[067] The at least one intermediate segment comprising at least one constituent monomer of the at least one first block and at least one constituent monomer of the at least one second block of the polymer may be a random polymer.

[068] In an embodiment, the at least one intermediate segment may be, for example, derived from constituent monomers of the at least one first block and of the at least one second block. For example, the at least one intermediate segment may be at least 85% derived from constituent monomers of the at least one first block and of the at least one second block, in a further embodiment at least 90% derived, for example at least 95%, and as a further example 100% derived.

[069] The at least one intermediate segment of the at least one block polymer has a glass transition temperature Tg ranging from the glass transition temperatures of the at least one first and second blocks.

[070] The at least one first and second blocks of the at least one block polymer of the composition have different glass transition temperatures.

[071] The glass transition temperatures indicated for the at least one first and second blocks of the at least one block polymer may be theoretical Tg values determined from the theoretical Tg values of the constituent monomers of each of the blocks. The theoretical Tg values may be found in a reference manual, such as, the Polymer Handbook, 3rd Edition, 1989, John Wiley, which is hereby incorporated by reference, according to the following relationship, known as Fox's law:

$$1/Tg = \sum_i (\varpi_i / Tg_i),$$

[072] ϖ_i being the mass fraction of the monomer i in the block under consideration and Tg_i being the glass transition temperature of the homopolymer of the monomer i.

[073] Unless otherwise indicated, the Tg values indicated for the at least one first and second blocks of the at least one block polymer are theoretical Tg values.

[074] The difference between the glass transition temperatures of the at least one first and second blocks of the at least one block polymer may be generally greater than 10°C, for example greater than 20°C, and as a further example greater than 30°C.

[075] In one embodiment, the at least one first block of the at least one block polymer may be chosen from:

[076] - a) a block with a Tg of greater than or equal to 40°C,

[077] - b) a block with a Tg of less than or equal to 20°C, and

[078] - c) a block with a Tg of between 20 and 40°C,

[079] and the at least one second block may be chosen from a block of category a), b) or c) that is different from the at least one first block.

[080] In the present invention, the expression:

[081] "between ... and ..." is intended to denote a range of values for which the limits mentioned are excluded, and

[082] "from ... to ..." and "ranging from ... to ..." are intended to denote a range of values for which the limits are included.

[083] <u>a) Block with a Tg of greater than or equal to 40°C</u>

[084] The block with a Tg of greater than or equal to 40°C of the at least one block polymer has, for example, a Tg ranging from 40 to 150°C, for example greater

than or equal to 50°C, for example ranging from 50°C to 120°C, and as a further example greater than or equal to 60°C, for example ranging from 60°C to 120°C.

[085] The block with a Tg of greater than or equal to 40°C may be a homopolymer or a copolymer.

[086] In the case where this block is a homopolymer, it may be derived from monomers wherein the homopolymers prepared from these monomers have glass transition temperatures of greater than or equal to 40°C. This first block may be a homopolymer comprising one type of monomer (for which the Tg of the corresponding homopolymer is greater than or equal to 40°C).

[087] In the case where the first block is a copolymer, it may be totally or partially derived from at least one monomer, the nature and concentration of which are chosen so that the Tg of the resulting copolymer is greater than or equal to 40°C. The copolymer may comprise, for example:

[088] - monomers wherein the homopolymers prepared from these monomers have Tg values of greater than or equal to 40°C, for example a Tg ranging from 40 to 150°C, for example greater than or equal to 50°C, for example ranging from 50°C to 120°C, and as a further example greater than or equal to 60°C, for example ranging from 60°C to 120°C, and

[089] - monomers wherein the homopolymers prepared from these monomers have Tg values of less than 40°C, chosen from monomers with a Tg of between 20 and 40°C and/or monomers with a Tg of less than or equal to 20°C, for example a Tg ranging from -100 to 20°C, in an embodiment less than 15°C, for example ranging from

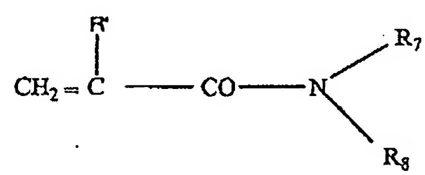
-80°C to 15°C, and as a further example less than 10°C, for example ranging from -50°C to 0°C, as described later.

[090] The monomers whose homopolymers have a glass transition temperature of greater than or equal to 40°C are chosen, for example, from the following monomers, also known as the main monomers:

[091] - methacrylates of formula $CH_2 = C(CH_3)\text{-}COOR_1$, wherein R_1 is chosen from linear and branched unsubstituted alkyl groups containing from 1 to 4 carbon atoms, such as methyl, ethyl, propyl and isobutyl groups, or R_1 is chosen froma C_4 to C_{12} cycloalkyl group,

[092] - acrylates of formula $CH_2 = CH\text{-}COOR_2$, wherein R_2 is chosen from a C_4 to C_{12} cycloalkyl group such as an isobornyl group or a tert-butyl group,

[093] - (meth)acrylamides of formula:



[094] wherein R_7 and R_8, which may be identical or different, are chosen from a hydrogen atom, and linear and branched C_1 to C_{12} alkyl groups such as n-butyl, t-butyl, isopropyl, isohexyl, isooctyl and isononyl groups; or R_7 is H and R_8 is a 1,1-dimethyl-3-oxobutyl group,

[095] and R' is chosen from H and methyl. Examples of monomers that may be mentioned include N-butylacrylamide, N-t-butylacrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide and N,N-dibutylacrylamide,

[096] - and mixtures thereof.

[097] Examples of main monomers are, for example, methyl methacrylate, isobutyl (meth)acrylate and isobornyl (meth)acrylate, and mixtures thereof.

[098] b) Block with a Tg of less than or equal to 20°C

[099] The block with a Tg of less than or equal to 20°C of the at least one block polymer has, for example, a Tg ranging from -100 to 20°C, in an embodiment less than or equal to 15°C, for example ranging from -80°C to 15°C, and in another embodiment less than or equal to 10°C, for example ranging from -50°C to 0°C.

[0100] The block with a Tg of less than or equal to 20°C may be a homopolymer or a copolymer.

[0101] In the case where this block is a homopolymer, it may be derived from monomers wherein the homopolymers prepared from these monomers have glass transition temperatures of less than or equal to 20°C. This second block may be a homopolymer comprising one type of monomer (for which the Tg of the corresponding homopolymer is less than or equal to 20°C).

[0102] In the case where the block with a Tg of less than or equal to 20°C is a copolymer, it may be totally or partially derived from at least one monomer, the nature and concentration of which may be chosen such that the Tg of the resulting copolymer is less than or equal to 20°C.

[0103] It may comprise, for example,

[0104] - at least one monomer whose corresponding homopolymer has a Tg of less than or equal to 20°C, for example a Tg ranging from -100°C to 20°C, in another embodiment less than 15°C, for example ranging from -80°C to 15°C, and in another embodiment less than 10°C, for example ranging from -50°C to 0°C, and

[0105] - at least one monomer whose corresponding homopolymer has a Tg of greater than 20°C, such as monomers with a Tg of greater than or equal to 40°C, for example a Tg ranging from 40 to 150°C, in another embodiment greater than or equal to 50°C, for example ranging from 50°C to 120°C, and in another example greater than or equal to 60°C, for example ranging from 60°C to 120°C, and/or monomers with a Tg of between 20 and 40°C, as described above.

[0106] In one embodiment, the block with a Tg of less than or equal to 20°C is a homopolymer.

[0107] The monomers whose homopolymer has a Tg of less than or equal to 20°C may be, for example, chosen from the following monomers, or main monomer:

[0108] - acrylates of formula $CH_2 = CHCOOR_3$, wherein R_3 is chosen from linear and branched C_1 to C_{12} unsubstituted alkyl groups, with the exception of the tert-butyl group, wherein at least one heteroatom chosen from O, N and S is (are) optionally intercalated,

[0109] - methacrylates of formula $CH_2 = C(CH_3)\text{-}COOR_4$, wherein R_4 is chosen from linear and branched C_6 to C_{12} unsubstituted alkyl groups, wherein at least one heteroatom chosen from O, N and S is (are) optionally intercalated,

[0110] - vinyl esters of formula $R_5\text{-}CO\text{-}O\text{-}CH = CH_2$, wherein R_5 is chosen from linear and branched C_4 to C_{12} alkyl groups,

[0111] - C_4 to C_{12} alcohol and vinyl alcohol ethers,

[0112] - N-(C_4 to C_{12})alkyl acrylamides, such as N-octylacrylamide,

[0113] - and mixtures thereof.

[0114] Examples of main monomers for the block with a Tg of less than or equal to 20°C include, for example, alkyl acrylates whose alkyl chain contains from 1 to 10 carbon atoms, with the exception of the tert-butyl group, such as methyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate, and mixtures thereof.

[0115] c) Block with a Tg of between 20 and 40°C

[0116] The block with a Tg of between 20 and 40°C of the at least one block polymer may be a homopolymer or a copolymer.

[0117] In the case where this block is a homopolymer, it may be derived from monomers (or main monomer) wherein the homopolymers prepared from these monomers have glass transition temperatures of between 20 and 40°C. This first block may be a homopolymer, comprising one type of monomer (for which the Tg of the corresponding homopolymer is between 20°C to 40°C).

[0118] The monomers whose homopolymer has a glass transition temperature of between 20 and 40°C may be, for example, chosen from n-butyl methacrylate, cyclodecyl acrylate, neopentyl acrylate and isodecylacrylamide, and mixtures thereof.

[0119] In the case where the block with a Tg of between 20 and 40°C is a copolymer, it may be totally or partially derived from at least one monomer (or main monomer) whose nature and concentration are chosen so that the Tg of the resulting copolymer is between 20 and40°C.

[0120] The block with a Tg of between 20 and 40°C may be a copolymer totally or partially derived from:

[0121] - main monomers whose corresponding homopolymer has a Tg of greater than or equal to 40°C, for example a Tg ranging from 40°C to 150°C, in an embodiment

greater than or equal to 50°C, for example ranging from 50 to 120°C, and in another embodiment greater than or equal to 60°C, for example ranging from 60°C to 120°C, as described above, and/or

[0122] - main monomers whose corresponding homopolymer has a Tg of less than or equal to 20°C, for example a Tg ranging from -100 to 20°C, in another embodiment less than or equal to 15°C, for example ranging from -80°C to 15°C, and in another embodiment less than or equal to 10°C, for example ranging from -50°C to 0°C, as described above.

[0123] The monomers may be chosen so that the Tg of the copolymer forming the first block is between 20 and 40°C.

[0124] Such main monomers may be chosen, for example, from methyl methacrylate, isobornyl acrylate and methacrylate, butyl acrylate and 2-ethylhexyl acrylate, and mixtures thereof.

[0125] In one embodiment, the proportion of the second block with a Tg of less than or equal to 20°C ranges from 10% to 85% by weight, for example from 20% to 70%, and as a further example from 20% to 50% by weight of the polymer.

[0126] However, each of the blocks of the at least one block polymer may contain in small proportion at least one constituent monomer of the other block.

[0127] Thus, the at least one first block of the at least one block polymer may contain at least one constituent monomer of the at least one second block, and vice versa.

[0128] Each of the at least one first and/or second blocks of the at least one block polymer may comprise, in addition to the monomers indicated above, at least one other

monomer known as additional monomers, which are different from the main monomers mentioned above.

[0129] The nature and amount of this or these additional monomer(s) may be chosen such that the block in which they are present has the desired glass transition temperature.

[0130] This additional monomer may be chosen, for example, from:

[0131] a) hydrophilic monomers such as:

[0132] - ethylenically unsaturated monomers comprising at least one carboxylic or sulphonic acid function, for example, acrylic acid, methacrylic acid, crotonic acid, maleic anhydride, itaconic acid, fumaric acid, maleic acid, acrylamidopropanesulphonic acid, vinylbenzoic acid, vinylphosphoric acid, and salts thereof,

[0133] - ethylenically unsaturated monomers comprising at least one tertiary amine function, for instance 2-vinylpyridine, 4-vinylpyridine, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate and dimethylaminopropylmethacrylamide, and salts thereof,

[0134] - methacrylates of formula $CH_2 = C(CH_3)\text{-}COOR_6$, wherein R_6 is chosen from linear and branched alkyl groups containing from 1 to 4 carbon atoms, such as methyl, ethyl, propyl and isobutyl groups, the alkyl group being substituted with at least one substituent chosen from hydroxyl groups (for instance 2-hydroxypropyl methacrylate and 2-hydroxyethyl methacrylate) and halogen atoms (Cl, Br, I or F), such as trifluoroethyl methacrylate,

[0135] - methacrylates of formula $CH_2 = C(CH_3)\text{-}COOR_9$, wherein R_9 is chosen from linear and branched C_6 to C_{12} alkyl groups wherein at least one heteroatom

chosen from O, N and S is (are) optionally intercalated, wherein the alkyl group is substituted with at least one substituent chosen from hydroxyl groups and halogen atoms (Cl, Br, I or F);

[0136] - acrylates of formula CH_2= $CHCOOR_{10}$, wherein R_{10} may be chosen from linear and branched C_1 to C_{12} alkyl groups substituted with at least one substituent chosen from hydroxyl and halogen atoms (Cl, Br, I or F), such as 2-hydroxypropyl acrylate and 2-hydroxyethyl acrylate; (C_1-C_{12})alkyl-O-POE (polyoxyethylene) with repetition of the oxyethylene unit 5 to 30 times, for example methoxy-POE; and a polyoxyethylenated group comprising from 5 to 30 ethylene oxide units

[0137] b) ethylenically unsaturated monomers comprising at least one silicon atom, such as methacryloxypropyltrimethoxysilane and methacryloxypropyl-tris(trimethylsiloxy)silane,

[0138] - and mixtures thereof.

[0139] Examples of additional monomers include acrylic acid, methacrylic acid, trifluoroethyl methacrylate, and mixtures thereof.

[0140] According to an embodiment, the at least one block polymer of the composition disclosed herein may be a non-silicone polymer, i.e., a polymer free of silicon atoms.

[0141] This or these additional monomer(s) generally represent(s) an amount of less than or equal to 30% by weight, for example from 1% to 30% by weight, as a further example from 5% to 20% by weight and as another example from 7% to 15% by weight, relative to the total weight of the first and/or second blocks.

[0142] In one embodiment, each of the at least one first and second blocks of the at least one block polymer comprises at least one monomer chosen from acrylic acid, acrylic acid esters, methacrylic acid, methacrylic acid esters, and mixtures thereof.

[0143] In one embodiment, each of the at least one first and second blocks of the at least one block polymer may be totally derived from at least one monomer chosen from acrylic acid, acrylic acid esters, methacrylic acid, and methacrylic acid esters.

[0144] In one embodiment, the block polymer disclosed herein is free of styrene. "Polymer free of styrene" means that the polymer contains less than 10% by weight, relative to the total weight of the polymer, for example, less than 5% by weight, as a further example less than 2% by weight and as another example less than 1% by weight, or does not contain at all any styrene monomer including styrene and styrene derivatives such as for instance methylstyrene, chlorostyrene or chloromethylstyrene.

[0145] The at least one block polymer of the composition disclosed herein may be obtained by free-radical solution polymerization according to the following preparation process:

[0146] - a portion of the polymerization solvent is introduced into a suitable reactor and heated until an adequate temperature for the polymerization is reached (typically ranging from 60 to 120°C),

[0147] - once this temperature is reached, the at least one constituent monomer of the at least one first block is introduced in the presence of some of the polymerization initiator,

[0148] - after a time T corresponding to a maximum degree of conversion of 90%, the at least one constituent monomer of the at least one second block and the rest of the initiator are introduced,

[0149] - the mixture is left to react for a time T' (ranging from 3 to 6 hours), after which the mixture is cooled to room temperature (25° C),

[0150] - the polymer dissolved in the polymerization solvent is obtained.

[0151] The term "polymerization solvent" means a solvent or a mixture of solvents. The polymerization solvent may be chosen, for example, from ethyl acetate, butyl acetate, alcohols such as isopropanol or ethanol, aliphatic alkanes such as isododecane, and mixtures thereof. In one embodiment, the polymerization solvent is a mixture of butyl acetate and isopropanol or isododecane.

[0152] <u>First Embodiment</u>

[0153] According to a first embodiment, the at least one block polymer of the composition disclosed herein comprises at least one (for example, one) first block with a Tg of greater than or equal to 40°C, as described above in a), and at least one (for example,one) second block with a Tg of less than or equal to 20°C, as described above in b).

[0154] The first block with a Tg of greater than or equal to 40°C of the at least one block polymer may be a copolymer derived from monomers wherein the homopolymer prepared from these monomers has a glass transition temperature of greater than or equal to 40°C, such as the monomers described above.

[0155] The second block with a Tg of less than or equal to 20°C may be a homopolymer derived from monomers wherein the homopolymer prepared from these

monomers has a glass transition temperature of less than or equal to 20°C, such as the monomers described above.

[0156] The proportion of the block with a Tg of greater than or equal to 40°C of the at least one block polymer ranges from 20% to 90%, for example from 30% to 80%, and as a further example from 50% to 70% by weight of the polymer. In one embodiment, the proportion of the block with a Tg of less than or equal to 20°C ranges from 5% to 75%, for example from 15% to 50%, and as a further example from 25% to 45% by weight of the polymer.

[0157] Thus, according to a first variant, the at least one block polymer of the composition disclosed herein may comprise:

[0158] - at least one first block with a Tg of greater than or equal to 40°C, for example having a Tg ranging from 70 to 110°C, which is a methyl methacrylate/acrylic acid copolymer,

[0159] - at least one second block with a Tg of less than or equal to 20°C, for example ranging from 0 to 20°C, which is a methyl acrylate homopolymer, and

[0160] - at least one intermediate segment which is a methyl methacrylate/acrylic acid/methyl acrylate copolymer.

[0161] According to a second variant, the at least one block polymer of the composition disclosed herein may comprise:

[0162] - at least one first block with a Tg of greater than or equal to 40°C, for example ranging from 70 to 100°C, which is a methyl methacrylate/acrylic acid/trifluoroethyl methacrylate copolymer,

[0163] - at least one second block with a Tg of less than or equal to 20°C, for example ranging from 0 to 20°C, which is a methyl acrylate homopolymer, and

[0164] - at least one intermediate segment which is a methyl methacrylate/acrylic acid/methyl acrylate/trifluoroethyl methacrylate random copolymer.

[0165] Second Embodiment

[0166] According to a second embodiment, the at least one block polymer of the composition disclosed herein comprises at least one first block having a glass transition temperature (Tg) of between 20 and 40°C, in accordance with the blocks described in c), and at least one second block having a glass transition temperature of less than or equal to 20°C, as described above in b), or a glass transition temperature of greater than or equal to 40°C, as described in a) above.

[0167] The proportion of the at least one first block with a Tg of between 20 and 40°C ranges from 10% to 85% by weight of the polymer, for example from 30% to 80%, and as a further example from 50% to 70%.

[0168] When the at least one second block is a block with a Tg of greater than or equal to 40°C, it may be, for example, present in an amount ranging from 10% to 85% by weight, for example from 20% to 70%, and as a further example from 30% to 70% by weight of the polymer.

[0169] When the at least one second block is a block with a Tg of less than or equal to 20°C, it may be, for example, present in an amount ranging from 10% to 85% by weight, for example from 20% to 70%, and as a further example from 20% to 50% by weight of the polymer.

[0170] The at least one first block with a Tg of between 20 and 40°C of the at least one block polymer may be a copolymer derived from monomers wherein the corresponding homopolymer has a Tg of greater than or equal to 40°C, and from monomers wherein the corresponding homopolymer has a Tg of less than or equal to 20°C.

[0171] The at least one second block with a Tg of less than or equal to 20°C or with a Tg of greater than or equal to 40°C may be a homopolymer.

[0172] The at least one block polymer of the composition disclosed herein comprises:

[0173] - at least one first block with a Tg of between 20 and 40°C, for example with a Tg of 25 to 39°C, which may be a copolymer comprising at least one methyl acrylate monomer, at least one methyl methacrylate monomer and at least one acrylic acid monomer,

[0174] - at least one second block with a Tg of greater than or equal to 40°C, for example ranging from 85 to 125°C, which may be a homopolymer composed of methyl methacrylate monomers, and

[0175] - at least one intermediate segment comprising at least one methyl acrylate, methyl methacrylate monomer, and

[0176] - at least one intermediate segment comprising methyl methacrylate, at least one acrylic acid monomer, and at least one methyl acrylate monomer.

[0177] The composition disclosed herein, for example, comprises from 0.1% to 60% by weight, for example from 0.5% to 50% by weight, and as a further example from

1% to 40% by weight, of the at least one block polymer relative to the total weight of the composition.

[0178] Solvent medium

[0179] The cosmetic composition disclosed herein comprises an organic solvent medium comprising at least one organic solvent.

[0180] The at least one organic solvent may be chosen from:

[0181] - ketones that are liquid at room temperature, such as methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, isophorone, cyclohexanone, or acetone;

[0182] - alcohols that are liquid at room temperature, such as ethanol, isopropanol, diacetone alcohol, 2-butoxyethanol, or cyclohexanol;

[0183] - glycols that are liquid at room temperature, such as ethylene glycol, propylene glycol, pentylene glycol, or glycerol;

[0184] - propylene glycol ethers that are liquid at room temperature such as propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, or dipropylene glycol mono-n-butyl ether;

[0185] - cyclic ethers such as γ-butyrolactone;

[0186] - short-chain esters (containing from 3 to 8 carbon atoms in total) such as ethyl acetate, methyl acetate, propyl acetate, isopropyl acetate, n-butyl acetate, isopentyl acetate, methoxypropyl acetate, or butyl lactate;

[0187] - ethers that are liquid at room temperature, such as diethyl ether, dimethyl ether, or dichlorodiethyl ether;

[0188] - alkanes that are liquid at room temperature, such as decane, heptane, dodecane, or cyclohexane;

[0189] - alkyl sulphoxides, such as dimethyl sulphoxide;

[0190] - aldehydes that are liquid at room temperature, such as benzaldehyde or acetaldehyde;

[0191] -heterocyclic compounds such as tetrahydrofuran;

[0192] - propylene carbonate or ethyl 3-ethoxypropionate; and

[0193] -mixtures thereof.

[0194] The solvent may be, for example, chosen from short-chain esters containing from 3 to 8 carbon atoms in total, such as ethyl acetate, methyl acetate, propyl acetate, isopropyl acetate, n-butyl acetate, isopentyl acetate, methoxypropyl acetate, or butyl lactate, and mixtures thereof.

[0195] The organic solvent medium, for example, has a polarity P ranging from 0.422 to 0.725.

[0196] The polarity is defined as a function of the solubility parameters according to the Hansen solubility space, according to the following relationship:

$$P = \sqrt{(\delta p^2 + \delta h^2)}/\delta t$$

[0197] - δh defines the specific forces of interaction (such as hydrogen bonding, acid/base bonding, donor/acceptor bonding, etc.);

[0198] - δp defines the Debye interaction forces between permanent dipoles and also the Keesom interaction forces between induced dipoles and permanent dipoles; and

[0199] - $\delta t = \sqrt{(\delta p^2 + \delta h^2 + \delta d^2)}$, δd defines the London dispersion forces derived from the formation of induced dipoles during molecular impacts.

[0200] The definition and calculation of the solubility parameters in the Hansen three-dimensional solubility space are described in the article by C.M. Hansen, "The three dimensional solubility parameters," *J. Paint Technol.*, 39, 105 (1967), which is hereby incorporated by reference.

[0201] When the solvent medium comprises a mixture of solvents, the polarity may be determined from the solubility parameters of the mixture, which are themselves determined from those of the compounds taken separately, according to the following relationships:

[0202]

$$\delta dmixt = \sum_i xi\, \delta di; \quad \delta pmixt = \sum_i xi\, \delta pi \quad \text{and} \quad \delta hmixt = \sum_i xi\, \delta hi$$

[0203] wherein xi is the volume fraction of the compound i in the mixture.

[0204] As organic solvents with a polarity ranging from 0.422 to 0.725, mention may be made, for example, of methyl acetate, ethyl acetate, isopropyl acetate, methoxypropyl acetate, butyl lactate, acetone, methyl ethyl ketone, diacetone alcohol, γ-butyrolactone, tetrahydrofuran, propylene carbonate, ethyl 3-ethoxypropionate and dimethyl sulphoxide, and mixtures thereof.

[0205] The organic solvent medium may represent from 10% to 95% by weight, for example from 15% to 80% by weight, and as a further example from 20% to 60% by weight, relative to the total weight of the composition.

[0206] Alternatively, the composition disclosed herein may, in one embodiment, comprise an aqueous medium.

[0207] <u>Additional film-forming polymer</u>

[0208] The composition may comprise, besides the at least one block polymer of the composition disclosed herein, at least one additional polymer, for example, a film-forming polymer. According to the present invention, the term "film-forming polymer" means a polymer that is capable, by itself or in the presence of at least one auxiliary film-forming agent, of forming a continuous film that adheres to a support, for example to keratin materials.

[0209] Among the film-forming polymers that may be used in the composition of the present invention, mention may be made of synthetic polymers, of free-radical type or of polycondensate type, and polymers of natural origin, and mixtures thereof.

[0210] The film-forming polymer may be chosen, for example, from cellulose-based polymers such as nitrocellulose, cellulose acetate, cellulose acetobutyrate, cellulose acetopropionate or ethylcellulose, or alternatively polyurethanes, acrylic polymers, vinyl polymers, polyvinylbutyrals, alkyd resins, resins derived from aldehyde condensation products such as arylsulphonamide-formaldehyde resins, for instance toluenesulphonamide-formaldehyde resin, and arylsulphonamide-epoxy resins.

[0211] Film-forming polymers that may be, for example, used include nitrocellulose RS 1/8 sec.; RS 1/4 sec.; 1/2 sec.; RS 5 sec.; RS 15 sec.; RS 35 sec.; RS 75 sec.; RS 150 sec.; AS 1/4 sec.; AS 1/2 sec.; SS 1/4 sec.; SS 1/2 sec.; SS 5 sec., sold by the company Hercules; the toluenesulphonamide-formaldehyde resins "KETJENTFLEX MS80" from the company Akzo or "SANTOLITE MHP" or "SANTOLITE MS 80" from the company Faconnier or "RESIMPOL 80" from the company Pan Americana, the alkyd resin "BECKOSOL ODE 230-70-E" from the company Dainippon,

the acrylic resin "ACRYLOID B66" from the company Rohm & Haas, and the polyurethane resin "TRIXENE PR 4127" from the company Baxenden.

[0212] The at least one additional film-forming polymer may be present in the composition disclosed herein in an amount ranging from 0.1% to 60% by weight, for example ranging from 2% to 40% by weight, and as a further example from 5% to 25% by weight, relative to the total weight of the composition.

[0213] Plasticizer

[0214] The composition may also comprise at least one plasticizer. In particular, mention may be made, alone or as a mixture, of the usual plasticizers, such as:

[0215] - glycols and derivatives thereof chosen from diethylene glycol ethyl ether, diethylene glycol methyl ether, diethylene glycol butyl ether or diethylene glycol hexyl ether, ethylene glycol ethyl ether, ethylene glycol butyl ether, and ethylene glycol hexyl ether;

[0216] - glycerol esters,

[0217] - propylene glycol derivatives and for example propylene glycol phenyl ether, propylene glycol diacetate, dipropylene glycol butyl ether, tripropylene glycol butyl ether, propylene glycol methyl ether, dipropylene glycol ethyl ether, tripropylene glycol methyl ether, diethylene glycol methyl ether and propylene glycol butyl ether,

[0218] - acid esters, for example carboxylic acid esters, chosen from citrates, phthalates, adipates, carbonates, tartrates, phosphates, and sebacates,

[0219] - oxyethylenated derivatives chosen from oxyethylenated oils, for example, plant oils chosen from castor oil; and

[0220] mixtures thereof.

[0221] The amount of plasticizer may be chosen by a person skilled in the art on the basis of his general knowledge, so as to obtain a composition with cosmetically acceptable properties. The plasticizer may be, for example, present in an amount of less than 20%, for example less than 15%, as a further example less than 10%, and as an additional example less than 5% by weight relative to the total weight of the composition. In one embodiment, the composition disclosed herein is free of plasticizer.

[0222] Dyestuff

[0223] The composition disclosed herein may also comprise at least one dyestuff chosen from water-soluble dyes and pulverulent dyestuffs, for instance pigments, nacres and flakes that are well known to those skilled in the art. The dyestuffs may be present in the composition in an amount ranging from 0.01% to 50% by weight and for example from 0.01% to 30% by weight relative to the weight of the composition.

[0224] The term "pigments" should be understood as meaning white or colored, mineral or organic particles of any shape, which are insoluble in the physiological medium and which are intended to color the composition.

[0225] The term "nacres" should be understood as meaning iridescent particles of any shape, produced for example by certain molluscs in their shell, or alternatively synthesized.

[0226] The pigments may be white or colored, and mineral and/or organic. Among the mineral pigments that may be mentioned are titanium dioxide, optionally surface-treated, zirconium oxide or cerium oxide, and also zinc oxide, iron oxide (black, yellow or red) or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue, and metal powders, for instance aluminium powder or copper

powder. Among the organic pigments that may be mentioned are carbon black, pigments of D & C type, and lakes based on cochineal carmine or on barium, strontium, calcium or aluminium.

[0227] The nacreous pigments may be chosen from white nacreous pigments such as mica coated with titanium or with bismuth oxychloride, coloured nacreous pigments such as titanium mica coated with iron oxides, titanium mica coated for example with ferric blue or chromium oxide, titanium mica coated with an organic pigment of the above-mentioned type and also nacreous pigments based on bismuth oxychloride.

[0228] The water-soluble dyes are, for example, beetroot juice or methylene blue.

[0229] The composition disclosed herein may also comprise at least one filler, for example in an amount ranging from 0.01% to 50% by weight and for example ranging from 0.01% to 30% by weight, relative to the total weight of the composition. The term "filler" should be understood as meaning colorless or white, mineral or synthetic particles of any shape, which are insoluble in the medium of the composition, irrespective of the temperature at which the composition is manufactured. These fillers serve for example to modify the rheology or the texture of the composition.

[0230] The at least one filler may be mineral or organic in any form, platelet-shaped, spherical or oblong, irrespective of the crystallographic form (for example leaflet, cubic, hexagonal, orthorhombic, etc.). Mention may be made of talc, mica, silica, kaolin, polyamide (NYLON®) powders (ORGASOL® from Atochem), poly-β-alanine powder and polyethylene powder, powders of polytetrafluoroethylene polymers (TEFLON®), lauroyllysine, starch, boron nitride, hollow polymer microspheres such as

those of polyvinylidene chloride/acrylonitrile, for instance EXAPANCEL® (Nobel Industrie) or acrylic acid copolymers (POLYTRAP® from the company Dow Corning) and silicone resin microbeads (for example TOSPEARLS® from Toshiba), elastomeric polyorganosiloxane particles, precipitated calcium carbonate, magnesium carbonate, magnesium hydrocarbonate, hydroxyapatite, hollow silica microspheres (SILICA BEADS® from Maprecos), glass or ceramic microcapsules, and metal soaps derived from organic carboxylic acids containing from 8 to 22 carbon atoms and for example from 12 to 18 carbon atoms, for example zinc, magnesium or lithium stearate, zinc laurate or magnesium myristate.

[0231] <u>Other additives</u>

[0232] The composition may also comprise other ingredients commonly used in cosmetic compositions. Such ingredients may be chosen from spreading agents, wetting agents, dispersants, antifoams, preserving agents, UV-screening agents, active agents, surfactants, moisturizers, fragrances, neutralizers, stabilizers, and antioxidants.

[0233] Needless to say, a person skilled in the art will take care to select this or these optional additional compound(s), and/or the amount thereof, such that the advantageous properties of the composition disclosed herein are not, or are not substantially, adversely affected by the envisaged addition.

[0234] The examples that follow illustrate the invention, in a non-limiting manner.

[0235] In the examples that follow, the Tg values indicated for the at least one first and second blocks are theoretical Tg values calculated in the manner defined above.

[0236] **Example 1: Preparation of a poly(methyl methacrylate)/ acrylic acid/methyl acrylate) polymer**

[0237] 100 g of butyl acetate were introduced into a 1 liter reactor and the temperature was then raised so as to pass from room temperature (25°C) to 90°C in 1 hour. 180 g of methyl methacrylate, 30 g of acrylic acid, 40 g of butyl acetate, 70 g of isopropanol and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (TRIGONOX® 141 from Akzo Nobel) were then added, at 90°C and over 1 hour.

[0238] The mixture was maintained at 90°C for 1 hour.

[0239] 90 g of methyl acrylate, 70 g of butyl acetate, 20 g of isopropanol and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane were then introduced into the above mixture, still at 90°C and over 1 hour.

[0240] The mixture was maintained at 90°C for 3 hours and then diluted with 105 g of butyl acetate and 45 g of isopropanol, and the mixture was then cooled.

[0241] A solution containing 40% polymer active material in a butyl acetate/isopropanol mixture was obtained.

[0242] A polymer comprising a poly(methyl methacrylate/acrylic acid) first block with a Tg of 100°C, a polymethyl acrylate second block with a Tg of 10°C and an intermediate segment which was a methyl methacrylate/acrylic acid/polymethyl acrylate random polymer was obtained.

[0243] This polymer had a weight-average mass of 52,000 and a number-average mass of 18,000, i.e., a polydispersity index I of 2.89.

[0244] It had a storage modulus E' equal to 90 MPa at 30°C and 0.1 Hz and a tgδ value of 0.33 at 30°C and 20 Hz.

[0245] **Example 2: Preparation of a poly(methyl methacrylate)/ acrylic acid/methyl acrylate) polymer**

[0246] 100 g of butyl acetate were introduced into a 1 liter reactor and the temperature was then raised so as to pass from room temperature (25°C) to 90°C in 1 hour. 150 g of methyl methacrylate, 30 g of acrylic acid, 30 g of methyl acrylate, 40 g of butyl acetate, 70 g of isopropanol and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (TRIGONOX® 141 from Akzo Nobel) were then added, at 90°C and over 1 hour.

[0247] The mixture was maintained at 90°C for 1 hour.

[0248] 90 g of methyl acrylate, 70 g of butyl acetate, 20 g of isopropanol and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane were then introduced into the above mixture, still at 90°C and over 1 hour.

[0249] The mixture was maintained at 90°C for 3 hours and then diluted with 105 g of butyl acetate and 45 g of isopropanol, and the mixture was then cooled.

[0250] A solution containing 40% polymer active material in a butyl acetate/isopropanol mixture was obtained.

[0251] A polymer comprising a poly(acrylic acid/methyl acrylate) first block with a Tg of 80°C, a polymethyl acrylate second block with a Tg of 10°C and an intermediate segment which was an acrylic acid/methyl acrylate/polymethyl acrylate random polymer was obtained.

[0252] This polymer had a weight-average mass of 50,000 and a number-average mass of 17,000, i.e., a polydispersity index I of 2.95.

[0253] It had a storage modulus E' equal to 12 MPa at 30°C and 0.1 Hz and a tgδ value of 0.54 at 30°C and 20 Hz.

[0254] **Example 3: Preparation of a poly(acrylic acid/methyl acrylate/methyl acrylate/trifluoroethyl methacrylate) polymer**

[0255] 100 g of butyl acetate were introduced into a 1 litre reactor and the temperature was then raised so as to pass from room temperature (25°C) to 90°C in 1 hour. 120 g of methyl methacrylate, 30 g of acrylic acid, 60 g of trifluoroethyl methacrylate, 40 g of butyl acetate, 70 g of isopropanol and 1.8 g of 2,5-bis(2-ethyl-hexanoylperoxy)-2,5-dimethylhexane (TRIGONOX® 141 from Akzo Nobel) were then added, at 90°C and over 1 hour.

[0256] The mixture was maintained at 90°C for 1 hour.

[0257] 90 g of methyl acrylate, 70 g of butyl acetate, 20 g of isopropanol and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane were then introduced into the above mixture, still at 90°C and over 1 hour.

[0258] The mixture was maintained at 90°C for 3 hours and then diluted with 105 g of butyl acetate and 45 g of isopropanol, and the mixture was then cooled.

[0259] A solution containing 40% polymer active material in a butyl acetate/isopropanol mixture was obtained.

[0260] A polymer comprising a poly(acrylic acid/methyl methacrylate/ trifluoroethyl methacrylate) first block with a Tg of 85°C, a polymethyl acrylate second block with a Tg of 10°C and an intermediate segment which was an acrylic acid/methyl acrylate/polymethyl acrylate/trifluoroethyl methacrylate random polymer was obtained.

[0261] This polymer had a weight-average mass of 53,000 and a number-average mass of 17 500, i.e., a polydispersity index I of 3.03.

[0262] It had a storage modulus E' equal to 3 MPa at 30°C and 0.1 Hz and a tgδ value of 0.34 at 30°C and 20 Hz.

[0263] **Example 4: Preparation of a poly(methyl methacrylate/methyl acrylate/acrylic acid) polymer**

[0264] 210 g of ethyl acetate were introduced into a 1 litre reactor and the temperature was then increased so as to pass from room temperature (25°C) to 78°C over 1 hour. 54 g of methyl methacrylate, 21 g of acrylic acid, 135 g of methyl acrylate and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (TRIGONOX® 141 from Akzo Nobel) were then added, at 78°C and over 1 hour.

[0265] The mixture was maintained at 90°C for 1 hour.

[0266] 90 g of methyl methacrylate, 90 g of ethyl acetate and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane were then introduced into the above mixture, still at 78°C and over 1 hour.

[0267] The mixture was maintained at 78°C for 3 hours and was then diluted with 150 g of ethyl acetate and cooled.

[0268] A solution containing 40% polymer active material in ethyl acetate was obtained.

[0269] The polymer obtained comprises a poly(methyl acrylate/methyl methacrylate/acrylic acid) first block with a Tg of 35°C, a poly(methyl methacrylate) second block with a Tg of 100°C and an intermediate segment which was a methyl methacrylate/acrylic acid/polymethyl acrylate random polymer.

[0270] This polymer had a weight-average mass of 141,000 and a number-average mass of 50,000, i.e., a polydispersity index I of 2.82.

[0271] **Example 5: Preparation of a poly(methyl methacrylate/methyl acrylate/acrylic acid) polymer**

[0272] 100 g of butyl acetate were introduced into a 1 litre reactor and the temperature was then raised so as to pass from room temperature (25°C) to 90°C over 1 hour. 50.4 g of methyl methacrylate, 21 g of acrylic acid, 138.6 g of methyl acrylate, 40 g of butyl acetate, 70 g of isopropanol and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (TRIGONOX® 141 from Akzo Nobel) were then added, at 90°C and over 1 hour.

[0273] The mixture was maintained at 90°C for 1 hour.

[0274] 90 g of methyl methacrylate, 70 g of butyl acetate, 20 g of isopropanol and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane were then introduced into the above mixture, still at 90°C and over 1 hour.

[0275] The mixture was maintained at 90°C for 3 hours and then diluted with 105 g of butyl acetate and 45 g of isopropanol, and cooled.

[0276] A solution containing 40% polymer active material in a butyl acetate/isopropanol mixture was obtained.

[0277] The polymer obtained comprises a poly(methyl acrylate/methyl methacrylate/acrylic acid) first block with a Tg of 35°C, a poly(methyl methacrylate) second block with a Tg of 100°C and an intermediate segment which was a methyl methacrylate/acrylic acid/polymethyl acrylate random polymer.

[0278] **Example 6: Nail varnish**

[0279] A nail varnish having the composition below was prepared:

Polymer of Example 1		23.8 g AM
Butyl acetate		24.99 g
Isopropanol		10.71 g
Hexylene glycol		2.5 g
DC Red 7 Lake		1 g
Hectorite modified with stearyldimethylbenzylammonium chloride (BENTONE® 27V from Elementis)		1.3 g
Ethyl acetate	qs	100 g

[0280] After application to the nails, this varnish was considered as having very good staying power and impact strength properties.

[0281] **Example 7: Nail varnish**

[0282] A nail varnish having the composition below may be prepared:

Polymer of Example 4		23.8 g	AM
Butyl acetate		24.99 g	
Isopropanol		10.71 g	
DC Red 7 Lake		1 g	
Hectorite modified with stearyldimethylbenzylammonium chloride (BENTONE® 27V from Elementis)		1.3 g	
Ethyl acetate	qs	100 g	

[0283] **Packaging**:

[0284] According to another aspect of the invention, there is provided a nail varnish product comprising : i) a container delimiting at least one compartment closed by a cap, and ii) a composition according to the invention received inside the compartment.

[0285] The container may be in the form of a bottle and can be formed, at least in part, of glass or of a material other than glass, such as at least one thermoplastic material, for example at least one thermoplastic material chosen from polypropylene and polyethylene, or a metal.

[0286] In a closed position of the container, the cap may be linked to the container by a threading arrangement.

[0287] As an alternative, the cap may linked to the container by an arrangement other than a threading arrangement, such as snap-fitting.

[0288] In one embodiment, the product comprises an applicator element which can be in the form of a brush having at least one tuft of bristles. As an alternative, the applicator element may be in a form other than a brush having at least one tuft of bristles, for example, in the form of a spatula or a foam pad.